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PRELIMINARY TESTS WITH SOME N-SUBSTITUTED p-ETHOXYBENZAMIDES FOR SYNERGISTIC ACTION IN ALLETHRIN FLY SPRAYS

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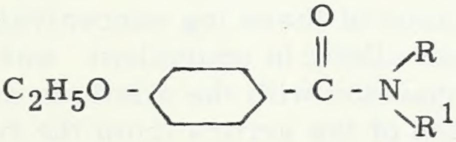
Several groups of compounds have been examined at the Beltsville, Md., laboratory in an effort to find new synergists for pyrethrins and allethrin.[1] In this study a group of p-ethoxybenzamides were tested for possible synergism with allethrin.

All the compounds were prepared by reacting p-ethoxybenzoyl chloride with various amines under suitable conditions. They may be represented by the general formula



$$C_2H_5O-C_6H_4-\overset{O}{\overset{\|}{C}}-N\begin{matrix}R\\R^1\end{matrix}$$

where R is hydrogen or an alkyl group and R^1 is an alkyl, aryl, cycloaliphatic, or heterocyclic group.

The compounds were incorporated in sprays, alone and in mixtures with 50 mg. of allethrin per deciliter of solvent, 1 part of acetone to 3 parts of refined kerosene. Insofar as practicable the mixtures were prepared in the proportion of 10 parts of adjunct to 1 part of allethrin. Even though acetone was used as an auxiliary solvent, the solubility of some compounds was so low that the concentration of the adjunct was lowered to 250 mg. per deciliter. In the sprays containing the adjunct alone the concentrations ranged from 333 to 2000 mg. per deciliter.

Allethrin standards were prepared in the same solvent mixture at 50, 100, and 200 mg. per deciliter. The allethrin used was from a distilled sample of high purity (94 percent by the hydrogenolysis method).

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[1] For reports on other groups of compounds see Bur. Ent. and Plant Quar. E-805, E-828, E-837, E-848, and E-869.

The tests were made by the Campbell turntable method on laboratory-reared adult house flies (Musca domestica L.). Approximately 110 flies averaging 2 to 3 days in age were used in each test. The mixed sprays were replicated four times on the same day with the same population of flies to avoid the danger of appreciable loss of acetone. The sprays containing the adjuncts alone were replicated twice. Since it was necessary to make the tests in several series, each with a different population of flies, the allethrin standard sprays were included in each series.

Since knock-down of flies is increased by the addition of acetone it is not reported; for the sprays containing allethrin it would be complete, or very nearly so, at the concentrations used without the presence of acetone. Mortality only was determined for each spray.

The adjuncts alone caused no or negligible mortality in 1 day at the concentrations used. The mean mortalities obtained with the sprays are given in table 1.

To determine whether synergism existed in the toxic action of the mixed sprays, the following procedure was used: In each series a regression equation for the allethrin standard was determined from the data by the method of probit analysis as described by Finney.[2] From this equation the logarithm of the allethrin equivalent was calculated for each of the four individual mortalities obtained with each spray. From an analysis of variance of these log concentrations the relative standard error of the mean allethrin equivalent was computed. The error contributed by comparison with the allethrin standard was computed. From a combination of the errors from the two sources the allethrin equivalent required to demonstrate synergism was determined, and reported in table 1.

The mean allethrin equivalents are given in table 1 and, since they are to be compared with the actual amount of allethrin in the mixtures--50 mg. per deciliter--they give, when divided by 50, expressions of relative toxicity.

Since the adjuncts were nontoxic at the concentrations used, any significant increase in toxicity over that of the allethrin in each mixture may be ascribed to synergistic action. Such an increase was clearly demonstrated for 7 mixtures; of the remaining 20, the increase for 14 was on the borderline of significance. Synergism could perhaps be demonstrated for the latter mixtures in more critical work. However, this would be of no practical importance, for in these preliminary tests the mixtures were less than 1.5 as toxic as allethrin.

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[2] Finney, D. J. Probit analysis. 318 pp. Cambridge. 1952.

The intensity of synergism was not very great for any of the effective materials. The effect was to raise toxicity to about 1.7 that expected for allethrin alone. This effect was obtained with the following synergists, all being among the higher disubstituted ethoxybenzamides:

N-Diamyl-p-ethoxybenzamide
N-Dibenzyl-p-ethoxybenzamide
N-Dibutyl-p-ethoxybenzamide
N-Butyl-4-ethoxybenzanilide
4-Ethoxy-N-ethylbenzanilide
p-Ethoxy-N-diisopropylbenzamide
p-Ethoxy-N-dipropylbenzamide

This intensity does not reach that of the best synergists for allethrin as determined by the same method, piperonyl butoxide and sulfoxide. In mixtures of similar proportion the effect with each of these was to raise toxicity to about three times that expected for allethrin alone.[3]

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[3] Gersdorff, W. A., and P. G. Piquett. A comparison of cyclethrin, allethrin, pyrethrins, and mixtures of piperonyl butoxide or sulfoxide with them in house fly sprays. Jour. Econ. Ent. (in press).

Table 1.--Joint toxic action against house flies of certain N-substituted *p*-ethoxybenzamides and allethrin. Concentration of allethrin 50 mg. and of amides 500 mg. per deciliter unless otherwise indicated. Four replicates.

Adjunct	Concentration at which tested alone	Mean mortality caused by mixture in 1 day	Mean allethrin equivalent
	Mg. per dl.	Percent	Mg. per dl.
Series 1			
Benzamide, *N*-butyl-*p*-ethoxy-	2000	31.4	55.7
p-ethoxy-*N*-ethyl-	2000	37.4	63.8
p-ethoxy-*N*-methyl-[1]	500	38.9	65.2
p-ethoxy-*N*-pentyl-	2000	37.2	63.7
p-ethoxy-*N*-propyl-	2000	35.3	61.5
Allethrin standard	200	90.8	198
	100	64.0	101
	50	24.3	48.7
Required to demonstrate synergism -------------		36.4	62.8
Equation for allethrin standard, Y = 3.381X - 1.427			
Heterogeneity factor, 1			
Series 2			
Benzamide, *N*-*sec*-amyl-*p*-ethoxy-	1000	34.4	64.9
N-*sec*-butyl-*p*-ethoxy-	2000	36.3	67.5
p-ethoxy-*N*-diethyl-	2000	37.2	68.9
p-ethoxy-*N*-isobutyl-	2000	33.8	64.3
p-ethoxy-*N*-dimethyl-	2000	28.9	57.3
Allethrin standard	200	85.9	194
	100	59.4	105
	50	21.2	47.3
Required to demonstrate synergism -------------		32.4	62.7
Equation for allethrin standard, Y = 3.121X - 1.064			
Heterogeneity factor, 1			

Table 1.--Continued

Adjunct	Concentration at which tested alone	Mean mortality caused by mixture in 1 day	Mean allethrin equivalent
	Mg. per dl.	Percent	Mg. per dl.
Series 3			
Benzamide, *N*-cyclohexyl-*p*-ethoxy-[1]	500	26.9	59.8
N-diamyl-*p*-ethoxy-	2000	45.5	82.6
N-dibutyl-*p*-ethoxy-	2000	54.2	94.8
p-ethoxy-*N*-diisopropyl-	2000	45.9	83.2
p-ethoxy-*N*-dipropyl	2000	42.2	78.2
Allethrin standard	200	88.2	188
	100	62.8	109
	50	15.5	46.1
Required to demonstrate synergism	------------	31.0	65.1
Equation for allethrin standard, Y = 3.667X - 2.144			
Heterogeneity factor, 8.5			
Series 4			
Benzamide, *N*-benzyl-*p*-ethoxy-	1000	31.2	54.6
N-dibenzyl-*p*-ethoxy-	2000	48.2	74.6
p-ethoxy-*N*-(3-isopropylaminopropyl)-	2000	35.4	59.4
p-ethoxy-*N*-(3-methoxypropyl)-	2000	35.4	59.4
p-ethoxy-*N*-(3-dimethylaminopropyl)-	2000	27.5	50.3
Allethrin standard	200	90.5	193
	100	67.4	106
	50	25.2	48.4
Required to demonstrate synergism	------------	37.9	62.3
Equation for allethrin standard, Y = 3.321X - 1.267			
Heterogeneity factor, 1			

Table 1.--Continued

Adjunct	Concentration at which tested alone	Mean mortality caused by mixture in 1 day	Mean allethrin equivalent
	Mg. per dl.	Percent	Mg. per dl.
Series 5			
Benzanilide, *N*-butyl-4-ethoxy-	2000	51.7	79.7
2'-chloro-4-ethoxy-	1000	32.2	56.0
4-ethoxy-[1]	500	31.8	54.9
4-ethoxy-*N*-ethyl	2000	51.4	79.2
Piperidine, 1-(*p*-ethoxybenzoyl)-	2000	41.8	66.2
Allethrin standard	200	88.3	176
	100	71.8	115
	50	22.7	45.7
Required to demonstrate synergism -------------		46.2	72.3
Equation for allethrin standard, Y = 3.342X - 1.309			
Heterogeneity factor, 17.8			
Series 6			
Benzanilide, 4'-chloro-4-ethoxy-[1]	333	24.4	50.0
Morpholine, 1-(*p*-ethoxybenzoyl)-	1000	31.5	58.2
Allethrin standard	200	84.7	170
	100	71.3	122
	50	19.6	44.5
Required to demonstrate synergism -------------		45.6	75.8
Equation for allethrin standard, Y = 3.253X - 1.225			
Heterogeneity factor, 28.4			

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[1] 250 mg. per deciliter.

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